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CHARACTERIZATION OF BORON CARBIDE WITH AN ELECTRONIC MICROPROBE

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16. Abstract Within the frame work of a study of heterogeneous materials (Matteudi et al., 1971; Matteudi and Verchery, 1972) thin deposits of boron carbide were characterized. Experiments using an electronic probe microanalyzer to analyze solid boron carbide or boron carbide in the form of thick deposits are described. Quantitative results on boron and carbon are very close to those obtained when applying the Monte Carlo- type correction calculations.					
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CHARACTERIZATION OF BORON CARBIDE WITH AN ELECTRONIC MICROPROBE

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Abstract

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The study of the composition of boron carbide with an electron microprobe, led us to examine the problems linked with the analysis of light elements such as boron and carbon. We have adopted the so-called classic ZAF method, eliminating however, the approximation generally used. We describe the experimental technique employed, and we give our results concerning the boron-carbon system.

1. Introduction

Within the framework of a study on heterogeneous materials [1, 2], we have been led to characterize thin deposits of boron carbide. Quantitative study with an electronic microanalyzer of very light elements such as boron and carbon, though made possible by the creation of synthetic pseudocrystals, still presents difficulties due in particular to the very strong absorption of X-rays and to the absence of sufficient theoretical data concerning correction methods.

We have investigated correction formulas applicable to the case of very light elements. The validity of our calculation has been verified by comparison to the Monte Carlo method.

2. Theoretical Study

Several techniques have already been published and rest mainly on the analysis of oxygen and carbon [3, 4, 5]. The Monte Carlo method seems to approach actuality with the maximum of precision [4]. As far

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2.2 Absorption Correction

The emergent X-ray intensity is given by relationship (6):

$$I = \int_0^{\infty} \varphi(\rho z) \exp[-\mu \cdot \rho z \cdot \operatorname{cosec} \theta] d(\rho z) \quad (6)$$

where $\varphi(\rho z)$ is the function of distribution of the ionization with depth. The probability of ionization of the back-scattered electrons being significant in the case of very light elements, it is not possible to neglect the function of ionization on the surface as it is usual to do. We have thus adopted the complete analytical expression, corresponding to relationship (2), which takes into account $\varphi(0)$. The function $f(\chi)$ is then written:

$$f(\chi) = \frac{1 + \frac{\varphi(0) h}{4 + \varphi(0) h} \cdot \frac{\chi}{\sigma}}{\left(1 + \frac{\chi}{\sigma}\right) \left(1 + \frac{h}{1 + h} \cdot \frac{\chi}{\sigma}\right)} \quad (7)$$

where $\chi = \mu \operatorname{cosec} \theta$.

From the energetic distribution of the back-scattered electrons, Duncumb [11] has calculated $\varphi(0)$ as a function of the mean atomic number Z , for various values of the excitation rate U . The variations $\varphi_0(Z, U)$ are shown in figure 1.

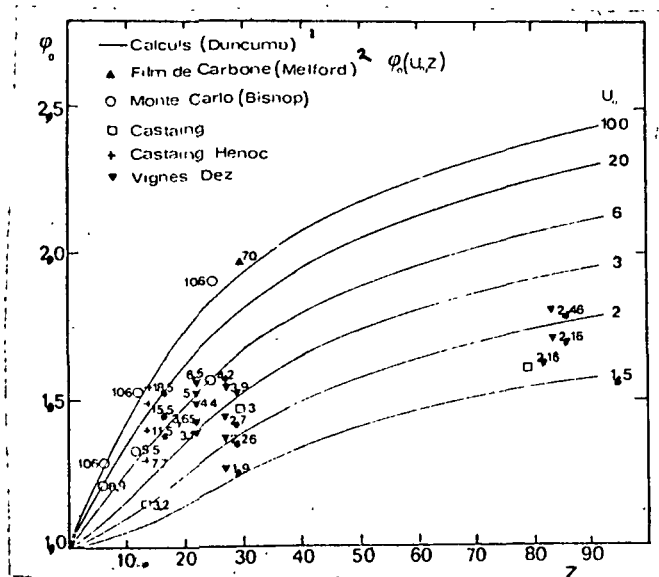


Figure 1. Variation of $\varphi(0)$ as a function of the mean atomic number and excitation rate.

Key: 1-Calculations (Duncumb)
2-Carbon film (Melford)

The SiC that we have used was not stoichiometric, but contained 33% carbon, which had been verified by chemical analysis and micro-analysis of the silicon.

3. Experimental Techniques

3.1. Analysis Conditions

We have investigated the most effective conditions of utilization of the CAMECA MS 46 microprobe (angle of emergence of 18°) for analysis of light elements. The characteristic lines of carbon $K_{\alpha C}$ (44.7 Å) and boron $K_{\alpha B}$ (67.6 Å) were analyzed by an ODPb crystal. The acceleration /29 voltage of the electrons varies from 5 to 35 kV. The probe current comprised between 100 and 150 nA. Background noise has been measured by shifting the spectrometer $\pm \lambda/5$ on both sides of the characteristic wave length. Use of the CAMECA anticontamination apparatus allows us to considerably reduce pollution by oil vapors from the secondary pump. Metallization of the sample was avoided by working in the vicinity of a coating of conductor paint. A proper surface is achieved by polishing with a diamond compound. A hard ultrasonic cleaning eliminates all trace of diamond.

3.2 Selection of Reference Solutions

For the carbon analysis, we have used a reference solution of diamond overlain by a fine coating of carbon conductor. The boron reference solution is a polycrystal of the Kawecky Society purified by electron bombardment. We have verified our analysis process by a method already adopted by Duncumb [4]. We calculate theoretically the variation of the intensity I emitted by a reference solution as a function of the high voltage E , and we compare it to the experimental emission. The theoretical calculation giving only a relative intensity, the two curves $I(E)$ were adjusted to 10 kV. Figures 3 and 4 present our results in the case of boron and carbon.

4. Analysis of Carbon and Boron

4.1 Study of B-C System

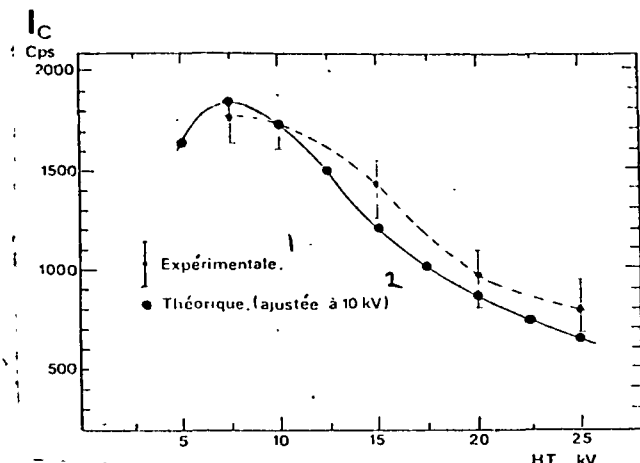


Figure 3. Intensity of carbon as a function of voltage.

Key: 1-Experimental 2-Theoretical (adjusted to 10 kV).

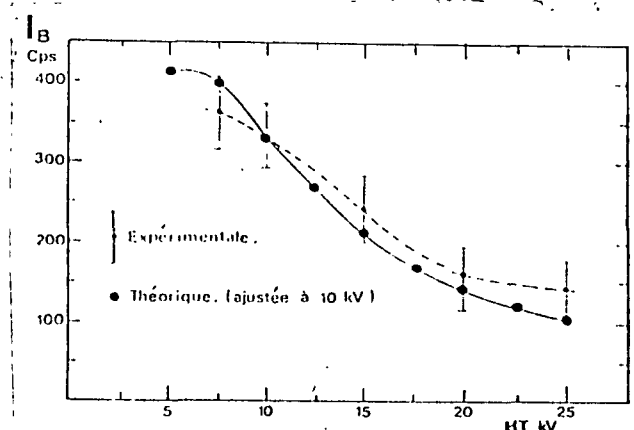


Figure 4. Intensity of boron as a function of voltage.

Key: 1-Experimental 2-Theoretical (adjusted to 10 kV).

There exist in the literature various phase diagrams of the boron-carbon system, which all present a continuous solid solution in the neighborhood of the compound B_4C [12].

For Samsonov [13], carbon was obtained from peritectic decomposition, which no longer appeared in the diagram of Elliott [14]. This one allows a very extensive scope of existence of B_4C , between 8 and 23% carbon (figure 5).

Nevertheless, after Amberger and Ploog [15], it seems that there was not a single carbon but several. Indeed, various compounds such as $B_{12}C$, B_7C , $B_{12}C_2$, $B_{5.66}C$, $B_{13}C_2$, and $B_{13}C_3$ have been observed separately.

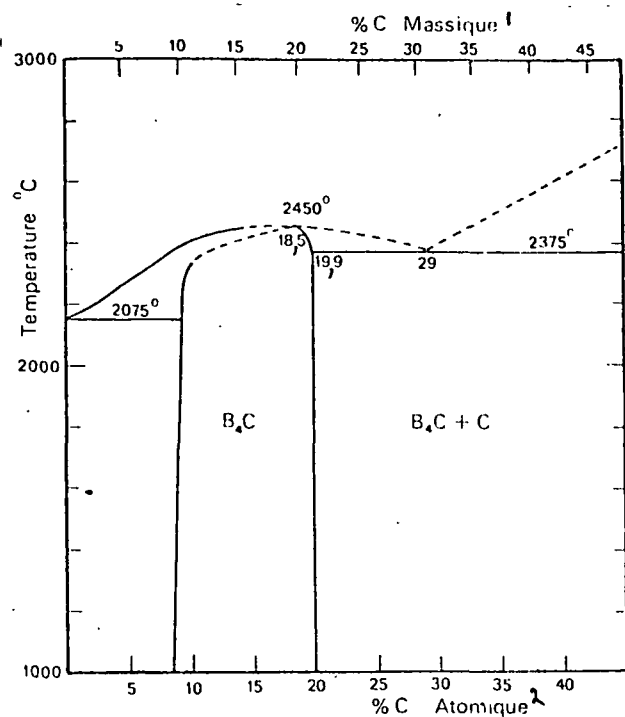


Figure 5. Boron-carbon phase diagram.

Key: 1-%C Massive 2-%C Atomic.

In comparing the respective structures of $B_{13}C_2$ and B_4C , which are known, we can interpret the formation of these various carbons in the following manner: the initial network of boron is β -rhombohedral, constituted by an icosahedral B_{12} fragment at each apex and of three boron atoms on the main diagonal. We can represent the boron by the symbol $B_{12}B_3$. The various carbons would be obtained by progressively replacing the boron atoms of the large diagonal by a carbon atom. We thus obtain for example $B_{13}C_2$ (2 carbon atoms) and $B_{12}C_3$ (B_4C , 3 carbon atoms). A solid solution then exists for each carbon, in progressively filling up the interstitial site situated at the center of the icosahedron. This allows us to take into account the existence of the other carbons obtained. We thus also obtain the limits of solubility proposed by Elliott: 8 to 23%. Finally, the observation made by Amberger ^{/30} and Ploog, according to which by adding carbon to $B_{13}C_3$ we do not obtain B_4C , but $B_{13}C_3$ + graphite mixture, not explained by the solid solution hypothesis. But if we allow that $B_{13}C_3$ is the carbon-saturated form of $B_{13}C_2$, the interstitial site being entirely occupied, this carbon can neither dissolve any more carbon nor convert into B_4C , of a different structure.

The hypothesis of the various carbons therefore appears more plausible, but nothing up to the present allows us to resolve this problem.

4.2 Analysis of Massive Boron Carbide

We have previously verified the validity of the application of our method to boron carbide. For this, we have compared our results (Figures 6 and 7) to those obtained by the Monte Carlo calculation perfected by Henoc [16, 17].

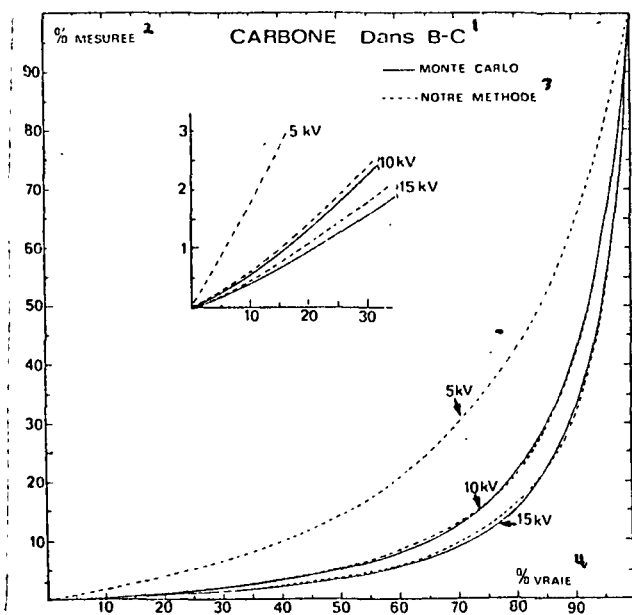


Figure 6. Comparison of experimental values of carbon to calculated values.

Key: 1-Carbon in B-C 2-% Measured 3-Our method 4-Actual %.

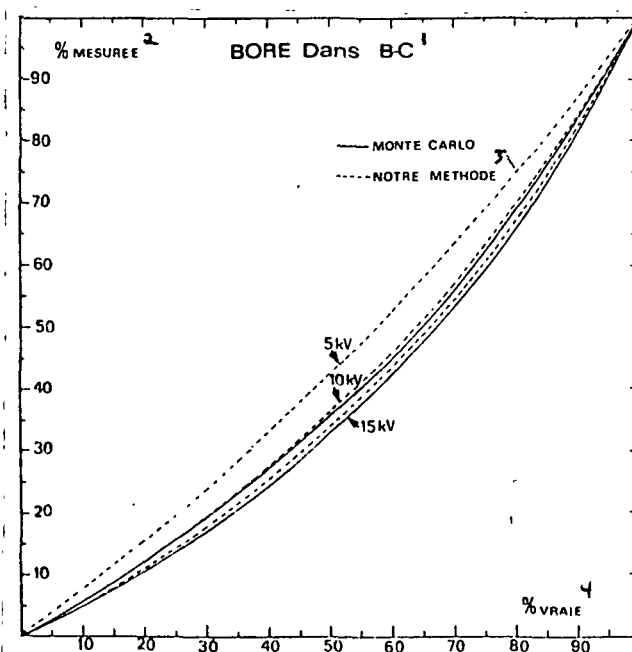


Figure 7. Comparison of experimental values of carbon to calculated values.

Key: 1-Boron in B-C 2-% Measured 3-Our method 4-Actual %.

4.2.1 Influence of the Chemical Bond

In the case of very light elements, valence electrons participate in the characteristic X-ray emission. The chemical bond, by disturbing the energetic level of the external electron coatings, modifies the X-ray wave length. This influence is all the more significant as the crystalline structures of the sample analyzed and the reference solution element are different. As figure 8 demonstrates, the variation $\Delta\lambda$ is 0.16 \AA (1 eV) between the tetrahedral diamond structure and the β -rhombohedral B_4C , which only differ by the presence of carbon atoms on the large diagonal of the rhombohedron (Figure 9).

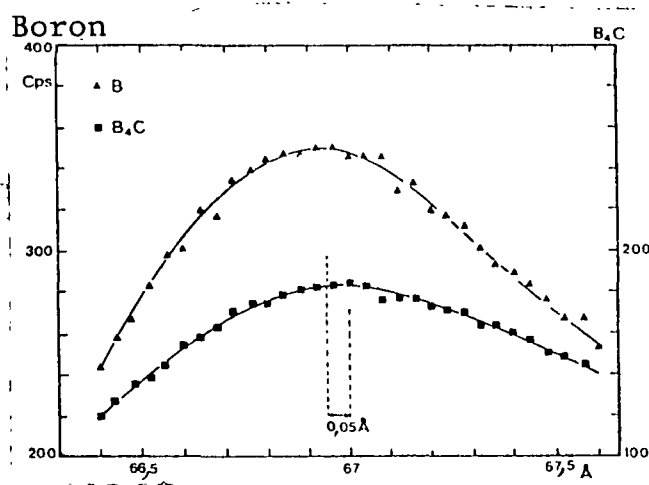


Figure 8. Variation of the boron structure.

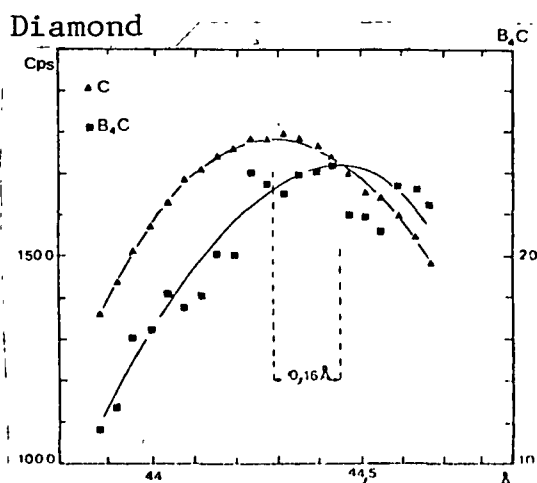


Figure 9. Variation of the diamond structure.

4.2.2 Selection of Absorption Coefficients

The very significant values of the absorption coefficients of very weak X-rays ($\lambda > 20 \text{ \AA}$) make experimental determinations delicate and less precise. There only exists very little data in this field: the most often used results are the semi-empirical values of Henke [18] limited to the discontinuities L which we have selected and which are in the case of boron and carbon:

$$\begin{aligned} \mu_{K_B}^B &= 3\,260 & \mu_{K_C}^C &= 2\,170 \\ \mu_{K_B}^C &= 6\,350 & \mu_{K_C}^B &= 35\,600 \end{aligned}$$

4.2.3 Carbon Analysis

The carbon X-ray being very much absorbed by boron, the corrections are significant as figure 6 demonstrates. We have given the histogram of all the analyses carried out on the samples of massive B_4C (figure 10).

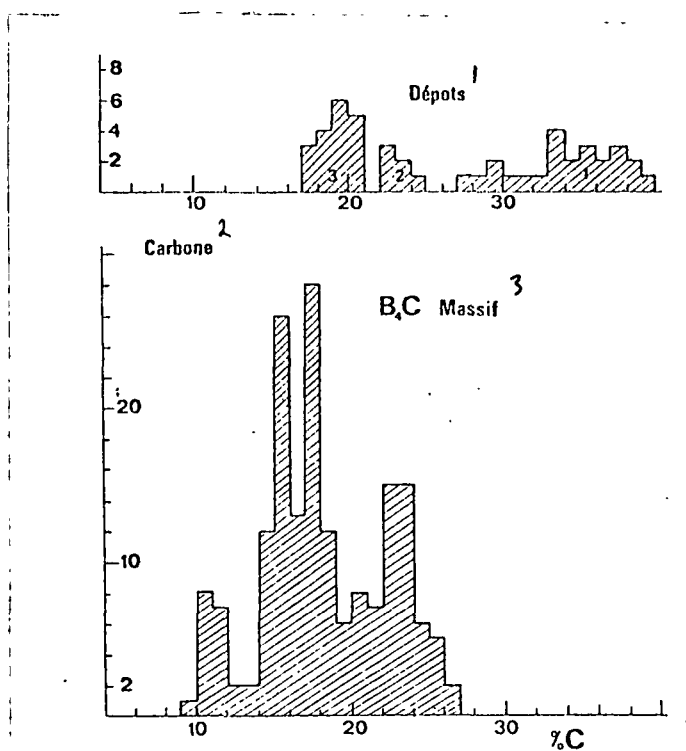


Figure 10. Histogram of the analyses carried out on samples of B_4C : per cent carbon.

Key: 1-Deposits 2-Carbon 3-Massive B_4C .

We note that the results, after correction, are situated within the limits of the scope of existence of B_4C ; the precision of the measurements made with the microprobe (1 to 2 % at the level of analysis be-

fore correction) do not allow us to better define the exact nature of the diagram.

4.2.4 Boron Analysis

In spite of a much larger dispersion, the analyses with boron are complementary to those of carbon (Figure 11).

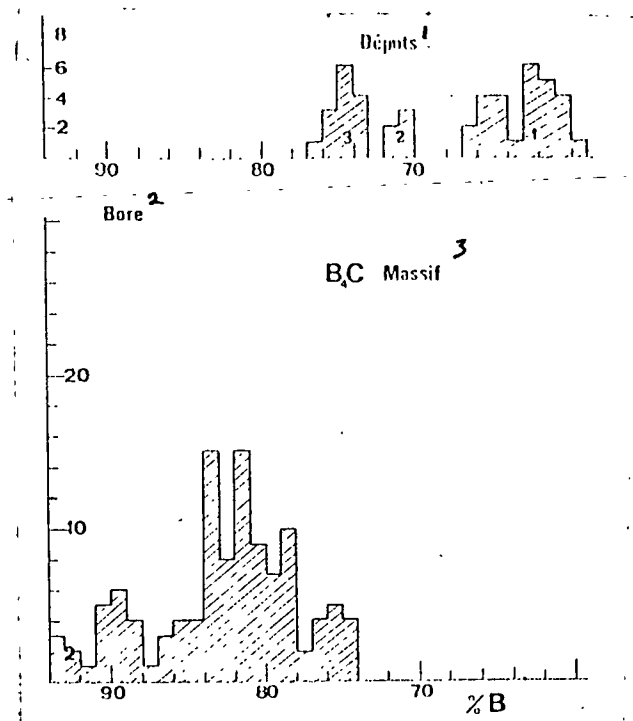


Figure 11. Histogram of the analyses carried out on samples of B_4C : per cent boron.

Key: 1-Deposits 2-Boron 3-Massive B_4C .

The analyses with boron and with carbon demonstrate therefore that commercial boron carbide¹ is not solely constituted of B_4C , but presents a variation of composition of 8 to 23%. Unfortunately, the structureless form of this carbon does not allow us to exactly define its nature.

4.3 Analysis of Boron Carbide Deposits

We have applied this method to the study of thick films ($>6 \mu$) of boron carbide prepared by vacuum evaporation. It is indeed advantageous to know the chemical composition of these deposits before using

¹"Touzart and Matignon" Society, 3, Rue Amyot, Paris, 5^e

them as reinforcement elements of composite plane materials [19]. From the point of view of microanalysis, these deposits have a sufficient thickness so that under certain conditions of high voltage (>15 kV), they behave like massive samples. The composition profiles obtained with carbon and with boron are represented respectively on figures 10 and 11. These deposits have been obtained through electron bombardment of the massive boron carbide previously analyzed.

Initial tests, using a graphite crucible, demonstrate a very clear increase of the carbon content (group 1 on figures 10 and 11), which can attain 40%.

It seems that this excess of carbon originates from the graphite crucible. Indeed, if we use a copper boat, the content is clearly much lower (groups 2 and 3).

We have also observed a development of the composition of the source during time by impoverishment with carbon. The deposits obtained at the start of fusion are richer in carbon (group 2) than the deposits at the end of fusion (group 3).

In a general manner, we have observed that deposits rich in boron offers a better mechanical firmness.

5. Conclusion

It is possible to use the electron microanalyzer probe to carry out analysis of massive boron carbide or its form of thick deposits. /32 The quantitative results with boron and with carbon are very close to those obtained by applying the Monte Carlo correction calculations.

Our method is applicable to all the very light elements O, N, C, and B. A systematic study of the carbides and oxides is currently underway and will in particular allow us to specify the value of certain absorption coefficients.

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